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# V-MCM-41 as selective catalyst for epoxidation of olefins and *trans*-2-hexene-1-ol

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## Abstract

Vanadium containing MCM-41(V-MCM-41) was synthesized by one pot synthesis and characterized by spectroscopic techniques. The oxidation of olefins such as 1-hexene, cyclohexene, cyclopentene, norbornene and *trans*-2-hexene-1-ol with tertiary butyl hydroperoxide (TBHP) in the presence of V-MCM-41 as catalyst in different solvents($CH_2Cl_2$, $CH_3CN$, $CH_3OH{\cdot}CHCl_3$) is described. It was found that V-MCM-41 in refluxing $CHCl_3$ was very reactive for epoxidation of *trans*-2-hexene-1-ol with 52% reactivity and 100% selectivity. Oxidation of *trans*-2-hexene-1-ol to the corresponding epoxide in the absence of solvent was successfully carried out with the enhancement of reactivity to 94%.

*Keywords:* V-MCM-41; Epoxidation; Olefins; *trans*-2-Hexene-1-ol

## 1. Introduction

The incorporation of transition metal ions into microporous or mesoporous molecular sieves is of considerable interest for catalytic applications. In fact, the development of ordered mesoporous materials containing different atoms in the pore walls has opened new possibilities for the use of mesoporous molecular sieves materials in the field of catalysis [1]. Since the discovery of mesoporous molecular sieves MCM-41 by Mobile [2,3] in 1992, it has attracted considerable attention for its potential use in adsorptive, separations and catalytic conversion of large molecules. MCM-41 pores has a regular hexagonal array in its mesopore structure with a high surface area. The pore size of MCM-41 can be systematically controlled from 20 to 100 Å by appropriate addition of surfactants during the synthesis [4].

Up to now, novel families of mesoporous silicates as M41S have been discovered in order to fill up the gap between microporous crystalline molecular sieves and macroporous supports [4–6]. MCM-41 analogue of metallosilicates has been prepared in the presence of heteroatoms such as Al [7], Ti [8], Mn [9,10], Fe [11], Cu [12], Ga [12], Zr [13], and Vanadium [14–16]. V-MCM-41 as well as other vanadium containing molecular sieves are reported to have catalytic activity in the ammoxidation of propane and xylenes, oxidation of butadiene to furan, and oxidative dehydrogenation of propane to propylene [17–19]. It was also used as catalyst for oxidation of methanol [20], hydroxylation of benzene [21], oxidation of lower alkanes [22] and oxidation of alcohols and aromatics [23].

In this study, we tried to prepare vanadium containing MCM-41 (V-MCM-41) for epoxidation of different olefins and alkeneols such as *trans*-2-hexene-1-ol and optimize the reaction conditions for maximum reactivity and selectivity toward the formation of a desired product. We have also tried to see the effect of different solvents on product distribution.

## 2. Experimental

### 2.1. Materials

All chemicals were purchased from Aldrich. Tertiary-butylhydroperoxide (TBHP; 80% in diethyl ether) was prepared from Merk chemical company.

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### 2.2. Physical measurements

Powder XRD patterns of samples were recorded on a diffractometer with Cu Kα radiation. Diffractometer type: PW1710 based with Tube anode Cu, Philips Analytical X-ray B.V. FT-IR measurements were performed on a FT-IR spectrophotometer PU9800 (Philips) KBr self-supported Pellet Technique. The oxidation products were analyzed by GC and GC-Mass using Philips PU 4400 chromatograph (1.5 m 3% OV-17 Column) and Varian 3400 chromatograph (25 m, DB-5 Column) coupled with a QP Finnigan mass INCOF 50 and 70 eV, respectively.

### 2.3. Preparation of MCM-41

MCM-41 was prepared according to the procedure described previously [24]. A typical procedure was as follow: 1.8 g of fumed silica was added to a solution prepared from dissolving 0.6 g of NaOH in 25 ml of water. The resultant mixture was stirred for 2 h, and then 1.9 g of cetyltrimethyl ammonium bromide (CTABr) in 20 ml of water was added to this solution and stirred for one more hour. The resulting reaction mixture which has the molar composition of 1 $SiO_2$, 7.5 $Na_2O$, 5.2 CTABr, 2500 $H_2O$ was kept over night and poured into the teflon lined stainless steel autoclave to make crystallization under static condition at 100 °C. The product was filtered, washed with distilled water, dried at 70 °C and calcined in air at 540 °C for 4 h.

### 2.4. Preparation of V-MCM-41

Vanadium containing MCM-41 (V-MCM-41) was prepared according to the procedure described previously [17]. A typical procedure was as follow; 0.6 g of fumed silica was added to a solution prepared by dissolving 0.13 g of NaOH in 6 ml of water. The resultant mixture was stirred for 2 h, then appropriate amount of vanadyl sulfate solution at various concentrations depending on Si/V ratio was added and stirred for another 3 h. Then 1.8 g of surfactant CTABr in 2 ml water was added to this solution and stirred for 2 h. The reaction mixture was kept at 100 °C for 3 days under hydrothermal condition. After filtration and washing with distilled water, it was dried at 70 °C and calcined in air at 120 °C for 3 h, and 440 °C for 3 h, and finally 550 °C for 5 h, respectively.

### 2.5. Oxidation of olefins

Oxidation reactions were performed in a stirring round bottom flask fitted with a water-cooled condenser. Reactions were carried out under atmospheric pressure at 65 °C with different solvens. Typically 0.2 g of catalyst (V-MCM-41) and 20 mmol of substrate in 5 ml of solvent, were added to the reaction flask with slow stirring. After a few minutes, TBHP (24 mmol) as oxidant was added to the reaction mixture at room temperature. After 6 h, the reaction mixture was filtered and products were analyzed by GC and GC Mass.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 1 shows the X-ray powder diffraction patterns of V-MCM-41 (Si/V = 16) sample after calcination. The calcined sample exhibits a very strong peak and four weak peaks. All five XRD reflections can be indexed on a hexagonal lattice. The XRD of calcined V-MCM-41 was completely consistent with V-MCM-41 [17].

The FTIR spectra of calcined MCM-41 and calcined V-MCM-41 (Si/V = 16) are shown in Fig. 2. The spectra of V-MCM-41 is closely resemble to the MCM-41, but the intensity of silanol group stretching (~3500 $cm^{-1}$) has been decreased in V-MCM-41. The asymmetric and symmetric stretching vibration bands appear at 1064 and 790 $cm^{-1}$ which are consistent with reported data [25]. The FT-IR observed band around 960 $cm^{-1}$, is often assigned to a lattice defect ions as M–O–Si type but this band is also observed in the spectram of calcined MCM-41. As reported by Chen and his coworker [26], this can also be assigned to a Si–O vibration in a Si–OH group in siliceous MCM-41.

The TGA pattern shows at least three distinct stages of weight loss. A weight loss due to the desorption of water amounting to 2.17% was observed between room temperature and 100 °C. The stage of 106–310 °C corresponds to a weight loss of 45.80% which can be ascribed to the decomposition of CTABr [27]. The weight loss of 7.64% from 310 to 600 °C can be assigned to coke calcinations and the loss of silanol groups (dehydroxylation) [28] (Fig. 3).

### 3.2. Vanadium containing MCM-41 as epoxidation catalyst

The oxidation of cyclohexene with TBHP in the presence of V-MCM-41 in refluxing different solvents;

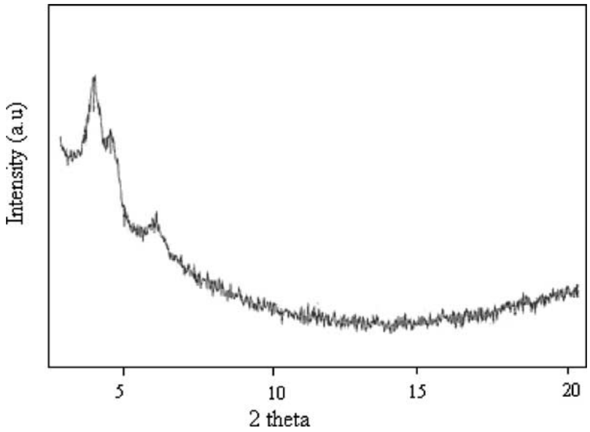


Fig. 1. XRD pattern of calcined Vanadium-containing MCM-41 (V-MCM-41).

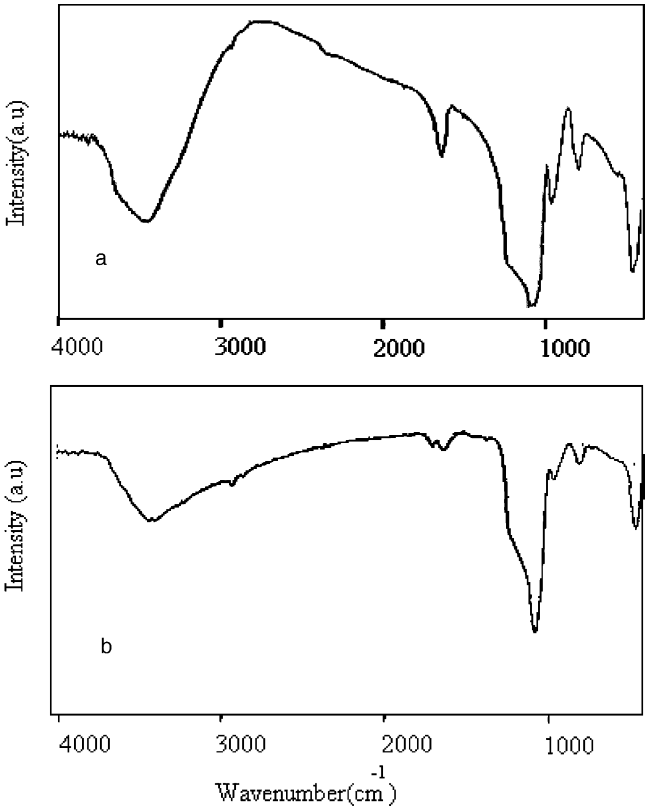


Fig. 2. Framework FTIR spectra of (a) calcinied MCM-41, (b) calcined V-MCM-41.

dicholoromethane, acetonitril, methanol and chloroform for 6 h results in the formation of several products as shown in Table 1 and Fig. 4. In the case of $CHCl_3$, the reactivity of oxidation of cyclohexene was 27% with 92% selectivity toward the formation of cyclohexene epoxide.

The oxidations results of *trans*-2-hexene-1-ol with TBHP in the presence of V-MCM-41 with and without solvent ($CHCl_3$) are given in Table 2 and Fig. 6.

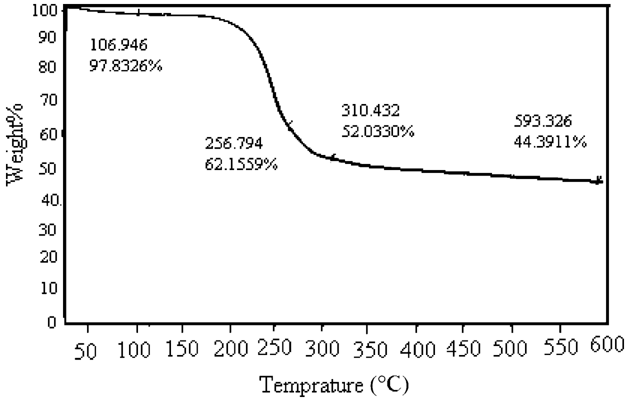


Fig. 3. TGA pattern of the sample V-MCM-41.

Table 1
Oxidation of cyclohexene with TBHP by V-MCM-41 in various solvents

| Run | Solvent | Conversion (%) | Selectivity | |
|---|---|---|---|---|
| | | | Epoxide | Others[a] |
| 1 | $CH_2Cl_2$ | 5 | 73 | 28 |
| 2 | $CH_3CN$ | 8 | 11 | 89 |
| 3 | $CH_3OH$ | 12 | 41 | 59 |
| 4 | $CHCl_3$ | 27 | 92 | 8 |

[a] Others are mixture of cyclohexenol, cyclohexenone and dicyclohexenether

Table 2
Oxidation of *trans*-2-hexene-1-ol by V-MCM-41 in various solvents

| Run | Solvent | Conversion (%) | Epoxide, selectivity (%) |
|---|---|---|---|
| 5 | $CH_3OH$ | 45 | 100 |
| 6 | $CHCl_3$ | 56 | 100 |
| 7 | *trans*-2-Hexene-1-ol | 94 | 100 |

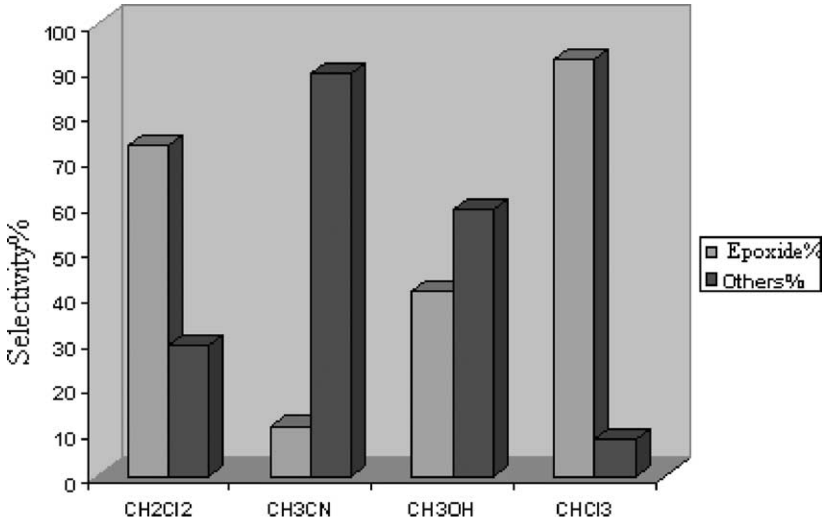


Fig. 4. Oxidation products distribution of cyclohexene in various solvents by V-MCM-41.

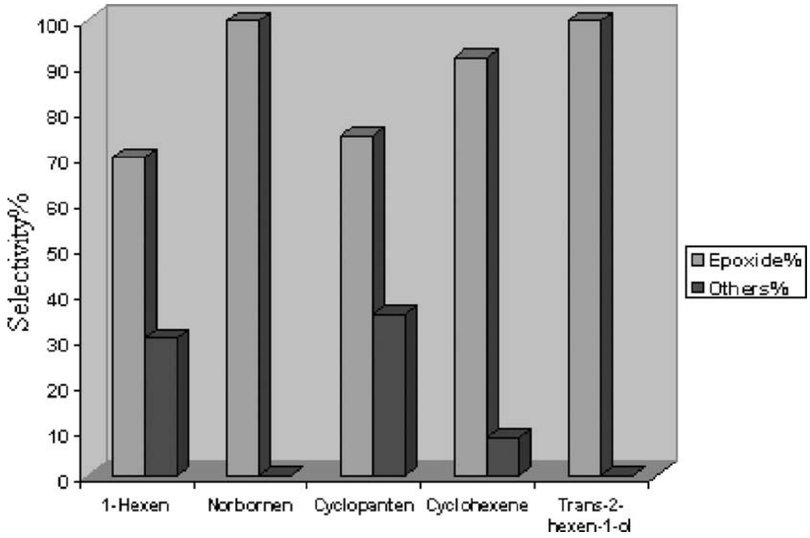


Fig. 5. Oxidation products distribution of olefins in $CHCl_3$ by V-MCM-41.

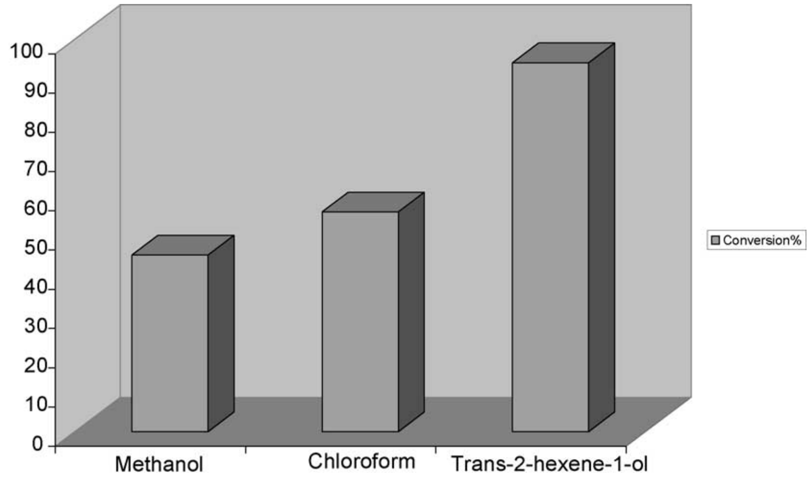


Fig. 6. Oxidation of *trans*-2-hexene-1-ol in methanol, chloroform and without using solvent.

In fact the use of microporous or mesoporous materials as catalyst for oxygenation of organic substrates with common oxidants like $O_2$, $H_2O_2$, and TBHP are of significant importance. In our recent publication, we reported that modified silicalite with molybdenum can successfully catalyze the epoxidation of *trans*-2-hexene-1-ol with TBHP [29]. Due to limited channel size of silicalites, medium and large size substrates will not be adsorbed within the channels in order to make complexation with metal centers. Therefore, we thought that using mesoporous incorporated vanadium materials such as MCM-41 would certainly provide larger rooms to accommodate for substrates of medium and large size to be complexed with the metal center.

In order to choose the best oxidation solvent, we investigated the oxidation of cyclohexene in several different solvents with a variety of dielectric constant either protic or aprotic. The results are shown in Table 1 and Fig. 4. It is evident that chloroform provides the best oxidation medium with highest reactivity and selectivity toward the formation of corresponding epoxides.

Table 3 and Fig. 5 presents the oxidation results of different olefins with TBHP as oxidant in chloroform. We have

Table 3
Oxidation of various alkenes with TBHP in the presence of V-MCM-41 in $CHCl_3$

| Run | Substrate | Conversion (%) | Yield (%) | |
|---|---|---|---|---|
| | | | Epoxide | Others[a] |
| 8 | 1-Hexene | 8 | 70 | 30 |
| 9 | Norbornene | 11 | 100 | – |
| 10 | Cyclohexene | 27 | 92 | 8 |
| 11 | Cyclopentene | 16 | 75 | 25 |
| 12 | *trans*-2-Hexene-1-ol | 56 | 100 | – |
| 13 | *trans*-2-Hexene-1-ol[b] | 2 | – | 100 |

[a] Others are mixture of alcohol, ketone and ether.

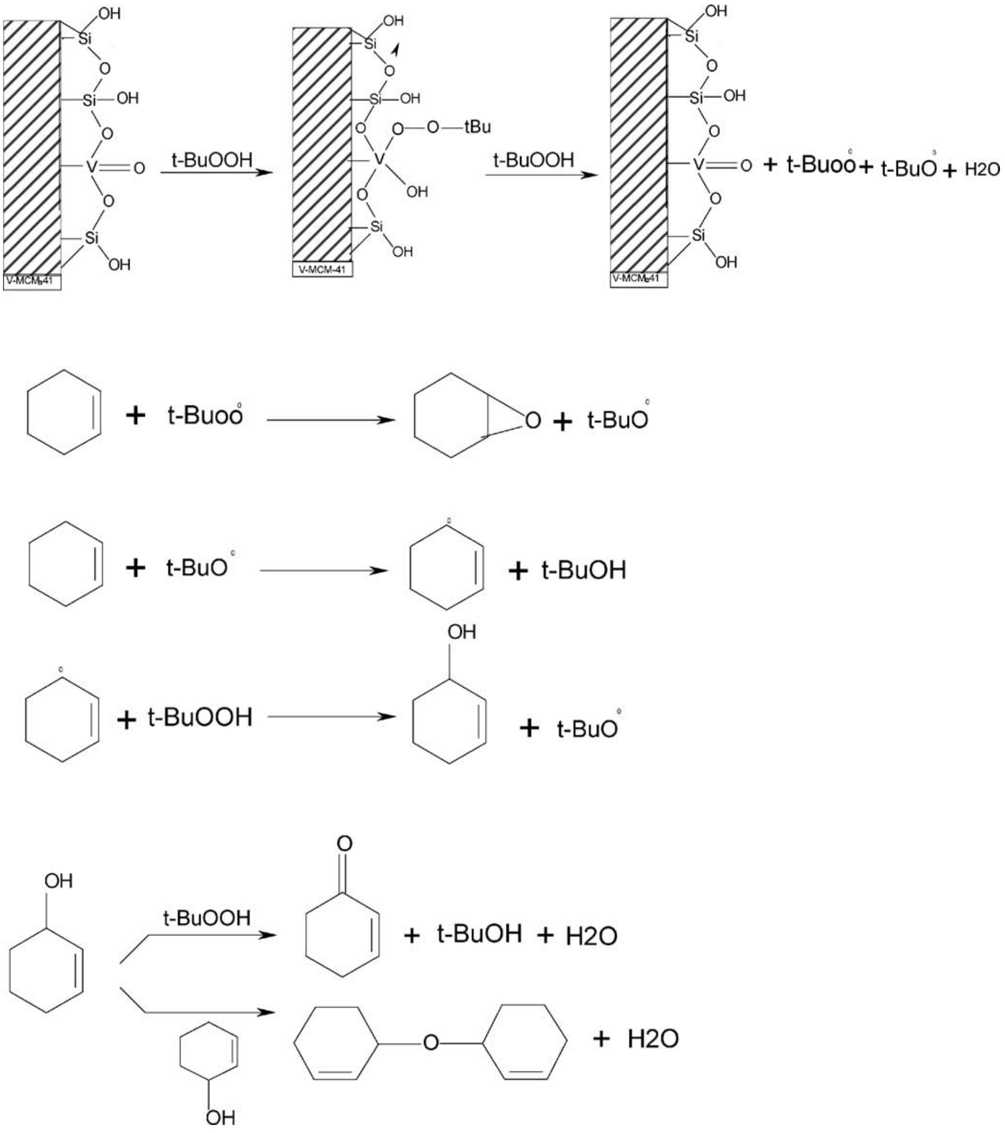
[b] In this case MCM-41 is catalyst.

included the oxidation results in the presence of MCM-41 (entry 13) in order do make the comparison with V-MCM-41 more convenient. According to the results, there is a drastic conversion difference between the normal olefins (entries 8–11) and allyl alcohol system (entry 12).

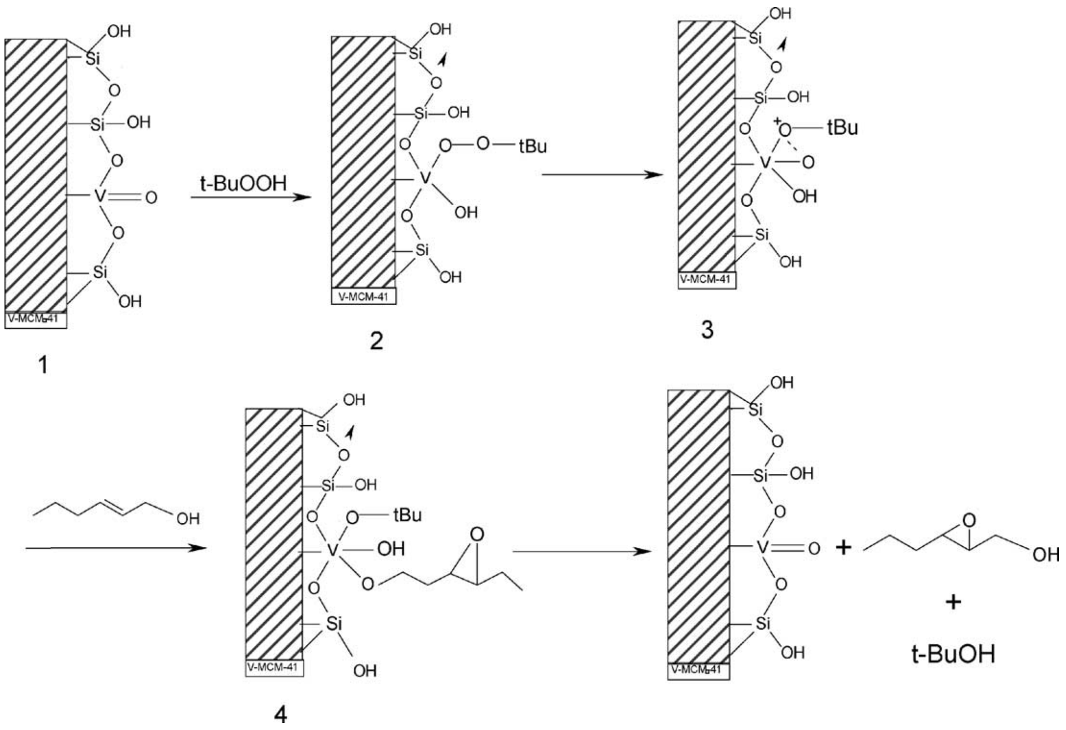
Alkene epoxidation by transition metal catalyzed reaction with alkylhydroperoxides is a well known reaction [30]. In the epoxidation reaction, more highly substituted alkenes react faster than less substituted alkenes [31–33]. Compared to 1-hexene (entry 8), the more substituted norbornene, cyclohexene, cyclopentene react faster by a factor 1.35–3.3 (entries 9–11).

In order to obtain a clear insight into the reaction mechanism, the involvement of V (V) in a one electron oxidation must be taken into consideration [34]. This process would promote the decomposition of TBHP to TBO$^\bullet$ and TBOO$^\bullet$... species (Scheme 1). Addition of TBOO$^\bullet$... to alkene double bond generates the corresponding radical. In the subsequent step, epoxide is formed with loss of TBuO$^\bullet$... species. These in turn abstracts the allylic hydrogen of alkenes to form the corresponding allylic radicals. Reaction of these radicals with TBHP would finally yield the mixture of alcohol, ketone and ether products (see Table 3).

Compared to the recent publication of Haller and his coworkers [35] which obtained cyclohexene oxide with 20.4% selectivity and 21.1% cyclohexene conversion, our result clearly indicates the higher efficiency of our system which led to the formation of cyclohexene oxide with 92% selectivity and 27% cyclohexene conversion. On the other hand, although Kumar and his coworkers [19] successfully carried out the epoxidation of cyclohexene with TBHP in the presence of V-MCM-41 with conversion 42.4%, the selectivity of oxidation toward the corresponding epoxide was 61% much lower compared to our result (Table 3, entry 10). This results clearly indicates the key role of $CHCl_3$ as oxidation solvent.



Scheme 1.



Scheme 2.

When we carried out the oxidation of *trans*-2-hexene-1-ol, the alkene conversion was increased to 56% with 100% selectivity toward the corresponding epoxide since allylic C–H oxidation products were not observed in this case; the operation of radical mechanism seems unlikely. Scheme 2 presents our proposed mechanism which was suggested on the basis of Sharpless proposed mechanism for the vanadium catalyzed epoxidation of allyl alcohol [36]. A vanadium (V) species such as 1 reacts with TBHP to give 2. Coordination of the second oxygen of the peroxide generates metal peroxide 3 via changing the vanadium coordination from tetrahedral to octahedral. Subsequent addition of *trans*-2-hexene-1-ol leads to the formation 3. Displacement of the epoxide with loss of tert-butyl alcohol regenerates the vanadium catalyst.

In order to see the effect of time on reaction rates, we examined the reaction times of 2, 4, 6, 8 h. The results are shown in Table 4, and Fig. 7. It can be seen that by increasing time from 2 to 4 and 6 h, the conversion of reaction increases from 20 to 56%. Since conversion reduction was observed above the 6 h, all reactions were carried out in 6 h.

Finally, it was found that the filtrate solution did not show any activity for oxidation and the filtered catalyst (V-MCM-41) was very active when it was used in another

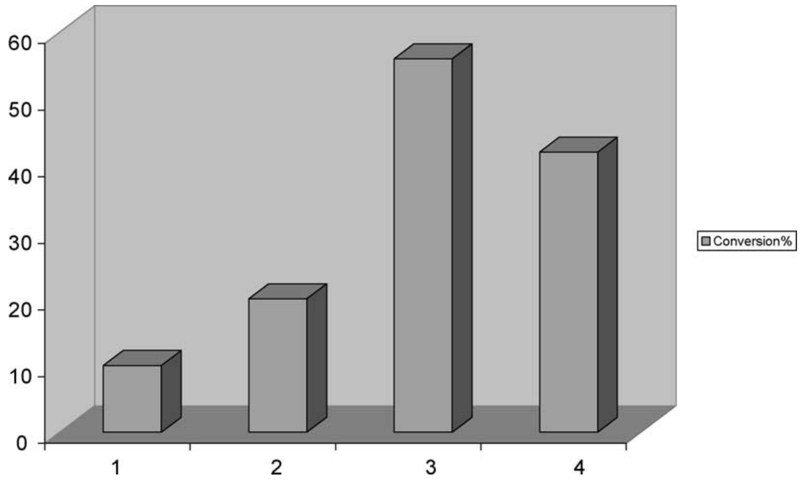


Fig. 7. Effect of time on oxidation of *trans*-2-hexene-1-ol in $CHCl_3$ with V-MCM-41.

Table 4
Effect of time on the oxidation of *trans*-2-hexene-1-ol with TBHP by V-MCM-41 in $CHCl_3$

| Run | Time (h) | Conversion (%) | Epoxide, selectivity (%) |
|---|---|---|---|
| 14 | 2 | 10 | 100 |
| 15 | 4 | 20 | 100 |
| 16 | 6 | 56 | 100 |
| 17 | 8 | 42 | 100 |

oxidation reaction. The observation of such activity in our catalysis system is promising.

## 4. Conclusion

The catalytic behavior of V-MCM-41 has been investigated in liquid phase oxidations of some olefins. The observation of high reactivity and selectivity in the case of *trans*-2-hexene-1-ol indicates the high efficiency of our catalysis system for the epoxidation of allylic alcohols. Moreover, the essential role of chloroform as oxidation solvent was determined in our investigation. The role of eliminating the solvent and studying other allylic alcohol epoxidation is currently under investigation in our laboratory.

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